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# THE SIMULATION OF A HIGH TEMPERATURE EQUILIBRIUM BY THE ACTION OF AN ELECTRODELESS DISCHARGE ON HYDROCARBONS*

by

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ABSTRACT

Some common hydrocarbons have been subjected to a 3000 watt R. F. electrodeless discharge. The distribution of the product approximates that calculated for a limited high temperature equilibrium along a temperature gradient. The presence of the predicted asphalt barrier is confirmed both from the appearance of the plasma for mixtures of hydrogen and methane and from the product distribution using hydrocarbons whose elemental composition falls in the asphalt region of the C-H-O ternary diagram computed by Dayhoff, et al. The free energy of formation of the solid product, of composition $C_{25}H_{10}$, over the temperature range 1000-1400°K is also estimated.

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## INTRODUCTION

Many workers have investigated the effect on hydrocarbons of high energy sources, such as arc and electrodeless discharges (1,2), pyrolysis (3,4) and the plasma jet (5,6). In each experiment acetylene is produced in fairly high yeild. In the equilibrium:

$$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$$

the reverse reaction is favored at low temperatures, but above about 1500°K the forward reaction predominates. Thus acetylene becomes a major product in the equilibrium of hydrocarbons, and in all the above experiments (1-6) the results can be explained by postulating a limited high temperature thermodynamic equilibrium.

Dayhoff, Lippincott and Eck (7,8) have written a computer program to calculate the concentration of the products of thermodynamic equilibrium for systems of up to 25 elements over a wide range of temperature and pressure, by minimizing the total free energy of the system (9). In a previous publication from this laboratory (10) it was shown that when a plasma is formed from organic oxygen compounds by means of an electrodeless discharge,

the major products are those predicted using this program, by assuming a temperature between 1000° and 1500°K.

In the work described here, a series of hydrocarbons are subjected to a 3000 watt R.F. electrodeless discharge; the products are analyzed and their concentrations are compared to the predicted concentrations assuming that a limited thermodynamic equilibrium determines the product formation.

## EXPERIMENTAL

The apparatus uses the same principles as that described in detail previously (10), although the power supply (3kV) and oscillator (7MHz) are different, enabling 3000 watts to be coupled into the plasma. The hydrocarbon samples used were either gases (of purity greater than 98%) from cylinders supplied by Matheson Scientific Inc. and Air Products and Chemicals Inc. or the vapours of analytical grade volatile liquids.

At low gas pressures the plasma is in the form of a glow discharge but as the pressure is raised, the glow localizes to a 'flame' plasma (10) with the consequent formation of a solid deposit. This is to be expected since the compositions of all of the compounds used fall in the asphalt region of the C-H-O ternary diagram (7,8,10). For saturated hydrocarbons, the transition from a glow discharge to a flame plasma occurs at a pressure of about 25 torr, and the working pressure used in the experiments was 30 torr, whereas for unsaturated hydrocarbons the transition

occurs at about 14 torr and the working pressure was 20 torr.

At the end of each experiment the apparatus was filled with 300 torr of helium to facilitate the analysis of the products by gas chromatography. This analysis was carried out using two gas chromatographs, a Varian Aerograph 1520B with a Linde 5B molecular sieve column using both thermal conductivity and flame detectors and a Perkin-Elmer 881 using a Parapak Q column with a flame detector. The former of these two columns was used to separate the light components, $H_2$, $CH_4$, $C_2H_6$ and $C_2H_2$, while the second column was used to determine the concentrations of the trace components such as the $C_3$ and $C_4$ hydrocarbons. Concentrations were determined from the areas under the peaks, calibration being carried out using a standard gas mixture made up by Matheson Scientific.

## COMPUTATIONS AND RESULTS

In all the computations which were performed the free energies for formation, $\Delta F_1^\circ$, of the simple hydrocarbons were those given by Rossini, et al. (11), while those of more complex molecules were calculated using the group contribution method of Van Krevelin and Chermin (12). Initially, to represent the solid product, the approximation was made which was described in the previous publication (10), namely that all the high molecular weight product was assumed to be a composite molecule of 100 isomers with the formula $C_{22}H_{12}$, and called asphalt; the free energy of formation of asphalt could then be calculated using the group contribution method (12). The

activation energy for the formation of graphite is considered to be so high that it is excluded from the computations (7,8,10).

These computations showed the formation of asphalt to be a major factor in determining the concentrations of the gaseous products. For a given temperature and for starting elemental compositions ranging from 20% carbon (methane) to 50% carbon (benzene), the concentrations of all the gases were shown to vary to a small degree, whereas that of asphalt varied considerably, accounting for the difference in total carbon content between the product gases and the reactant gas; this is illustrated in Figure I.

The gases used to determine the initial C:H ratios and their elemental compositions are shown in Table I, and the measured concentrations of the major products as determined using a gas chromatograph with the molecular sieve column and temperature programming to 300°C are shown in Table II. It is seen that the change in concentration of all these major components is insignificant over the five elemental compositions investigated. Qualitatively these results may be explained using the computed C-H-O ternary diagram (10); asphalt is deposted until the C:H ratio reaches the asphalt threshold. Since at this point all the gases have the same C:H ratio the resultant gases would be expected to be present in the same proportions if the species in the plasma were the same.

The pattern of concentrations of the minor products also varies only slightly for C-H elemental compositions from 20% to 50% of carbon, and this is illustrated in Figure II which shows the gas chromatograms of the products separated on a Parapak Q column with temperature programming to 170°C. It is seen that these five chromatograms are almost identical, which shows that the reactant gases are almost totally decomposed in the plasma. In the set of peaks due to the $C_3$ hydrocarbons, it can be seen that for the propane plasma product (C) the intensities of the peaks due to propane and propylene are reversed compared to those for the propylene plasma product (D); however, the difference is so small that it is calculated less than 0.01% of the starting gas is left unreacted. It is also of interest that although acetylene is formed in higher yield than ethane and ethylene, both propane andpropylene are formed in higher yield than propyne, which is seen in Figure II as a small shoulder at the base of the propane peak. At temperatures which would cause acetylene to predominate over ethylene and ethane, propyne should be present at a concentration of two orders of magnitude greater than either propane or propylene.

The formation of the minor products must be dominated by some factor besides thermodynamic equilibrium since the minor products are all present in far greater concentration than is computed for any temperature above room temperature. Figure III shows how the total equilibrium concentration of the hydrocarbons from $C_1$ to $C_5$ varies with the number of carbon atoms present in the molecules, and except for the two smallest carbon numbers, where acetylene becomes favored over methane at high temperatures, the logarithm of the sum of all

the mole fractions, $\sum n_i$, of the hydrocarbons with a given number of carbon atoms varies monotonically with the carbon number. However experimentally it is found that hydrocarbons with an even number of carbon atoms tend to predominate over those with an odd number; this is illustrated in Figure IV. Since the sensitivity of the flame ionization detector is roughly proportional to the carbon content of the hydrocarbon under investigation (13), the total area, A, under the peaks for each set of hydrocarbons with a given carbon content is divided by the carbon number, N, to give a measure to the total number of hydrocarbons with a given carbon content. Superimposed on the general downward trend is a clear indication that even carbon-numbered compounds predominate over those with an odd carbon number. It is interesting to note that Oro and Han (4), when pyrolyzing methane at 1000°C over silica gel, found that even numbered carbon compounds predominated, especially in arene formation, while Davis and Libby (14) who subjected solid methane at 77°K to gamma-ray radiolysis, found that there was a predominance of even carbon-numbered olefins. This may be connected with the fact that the $C_2$ radical has been identified spectroscopically as one of the major constituents in plasmas formed by the action of spark and glow discharges on methane (15).

It is of some importance that the minor compounds are present in greater rather than smaller concentrations than expected; this indicates that the build-up of large molecules is fairly easily achieved by the species present in the plasma. The species which have been

shown spectroscopically to be present in comets, e.g., H, CH and $C_2$ (16), have also been shown to be present in these plasmas (15). Urey (17), Whipple (18) and Oro (19) have suggested that the terrestral capture of non-volatile meteorite matter and cometary collisions may account for a large proportion of the organic compounds on the Earth. The present investigation shows that the concentrations of hydrocarbons may have accumulated above their equilibrium value by a similar mechanism.

The composition of the solid product on the walls of the reaction tube was found to be better approximated by a composition $C_{25}H_{10}$ rather than $C_{22}H_{12}$. The problem arose of what free energy of formation to use for asphalt of this composition, and a range of values was tried, from 140 to 320 k-cals/mole at a temperature of 1000°K, and from 200 to 380 k-cals/mole at 1400°K. Figure V shows how the computed concentrations of the major products change with these free energies of formation using composition A (methane). At very low values of $\triangle F^o_{asphalt}$ nearly all the carbon in the system is found in the asphalt and the mole fractions, $n_i$, of the other hydrocarbons, i, is too low, while at high values of $\triangle F^o_{asphalt}$, the concentration of asphalt becomes much smaller than is measured experimentally; the true value must take an intermediate value. The measured concentration of methane is best explained using $\triangle F^o_{asphalt}$ = 270 k-cals/ mole at 1100°K, while that of acetylene corresponds to $\Delta F^o_{asphalt}$ = 345 k-cals/mole at 1350°K. It is therefore suggested that products are formed in their equilibrium concentrations along the temperature gradient from the center of the plasma, the final product distribution being

determined by the inability of the molecules to overcome the activation energies involved at temperatures lower than 1000°K. This is the same process that was suggested in the previous publication from this laboratory on the distribution of reaction products from C-H-O plasmas (10).

Using values for $\Delta F^{o}_{asphalt}$ of 240 k-cals/ mole at 1000°K, 300 k-cals/mole at 1200°K and 360 k-cals/mole at 1400°K, computations were performed for various mixtures of methane and hydrogen in order to find where the asphalt barrier on the C-H-O ternary diagram cuts the C-H axis. For temperatures between 1100° and 1400°K, and for pressures between 20 and 100 torr, this threshold is found in the range 80% $H_2$: 20% $CH_4$ for low temperatures and 95% $H_2$: 5% $CH_4$ for high temperatures, see Figure VI. This corresponds the region on the C-H axis of the ternary diagram between 2% and 8% of carbon.

Experimentally it was found that when a mixture of methane and hydrogen was subjected to the discharge, the plasma changed from a glow discharge to a flame plasma as the proportion of methane was increased. For high ratios of hydrogen to methane, the pressure in the reaction tube would have to be raised above the normal value of 30 torr before this transition would occur. Experimentally the measured rates of hydrogen and methane flow were kept constant, while the total pressure was increased until the transition from a glow discharge to a flame plasma occured. The onset pressure of the flame plasma is plotted against various methane flow rates for a constant flow rate of hydrogen in Figure VII. It

is seen that a flame plasma could not be formed at any pressure below a certain flow rate of methane. The ratio of the flow rates of hydrogen and methane for this point was exactly 10:1 corresponding to a composition of 4% carbon and 96% hydrogen. In this fashion it is verified that a flame plasma corresponds to the formation of solid products in the discharge, and that the value for the asphalt threshold determined in this manner falls in the computed range of values.

The carbon to hydrogen ratio of the gaseous products is approximately 12% carbon and 88% hydrogen, which should also correspond to the composition at the asphalt threshold. The significance in the difference in these figures and the values determined above may be understood in terms of the temperatures at the relevant reaction zones in the plasma. The temperature at the center of the plasma is greater than at the edges, and Figure VI shows that the asphalt threshold shifts to a higher carbon percentage as the temperature is reduced. Thus it is to be expected that the two methods would give different values for the asphalt threshold, corresponding to the temperatures in the regions of the plasma where the reactions are occurring.

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TABLE I

Compounds Used and Their Elemental Compositions

| Compound | Composition | % Carbon | % Hydrogen |
|---|---|---|---|
| Methane | A | 20 | 80 |
| Ethane | B | 25 | 75 |
| Propane | C | 27.3 | 72.7 |
| Propylene | D | 33.3 | 66.7 |
| Benzene | E | 50 | 50 |

TABLE II

Concentrations of Major Components

| Composition | $H_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_2H_2$ |
|---|---|---|---|---|---|
| A | 73.3% | 15.4% | 0.9% | 2.3% | 8.0% |
| B * | 75.0 | 14.0 | 1.0 | 3.0 | 7.0 |
| C | 73.4 | 15.3 | 0.8 | 2.9 | 7.7 |
| D | 79.3 | 11.1 | 0.8 | 1.7 | 7.1 |
| E | 77.1 | 13.5 | 1.5 | 1.4 | 6.6 |

* - Estimated

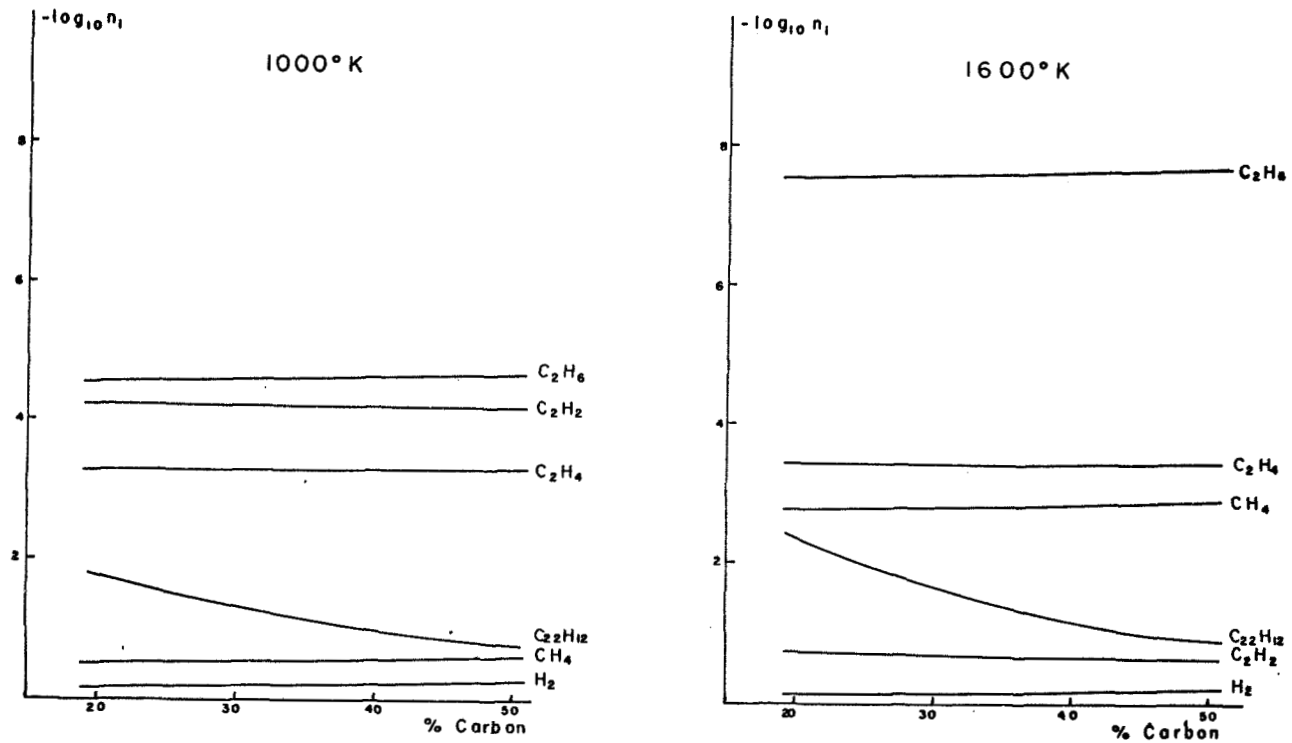
-log10 ni
1000° K
8
6
4
2
C2H6
C2H2
C2H4
C22H12
CH4
H2
20
30
40
50
% Carbon
-log10 ni
1600° K
8
6
4
2
C2H6
C2H4
CH4
C22H12
C2H2
H2
20
30
40
50
% Carbon

Figure 1

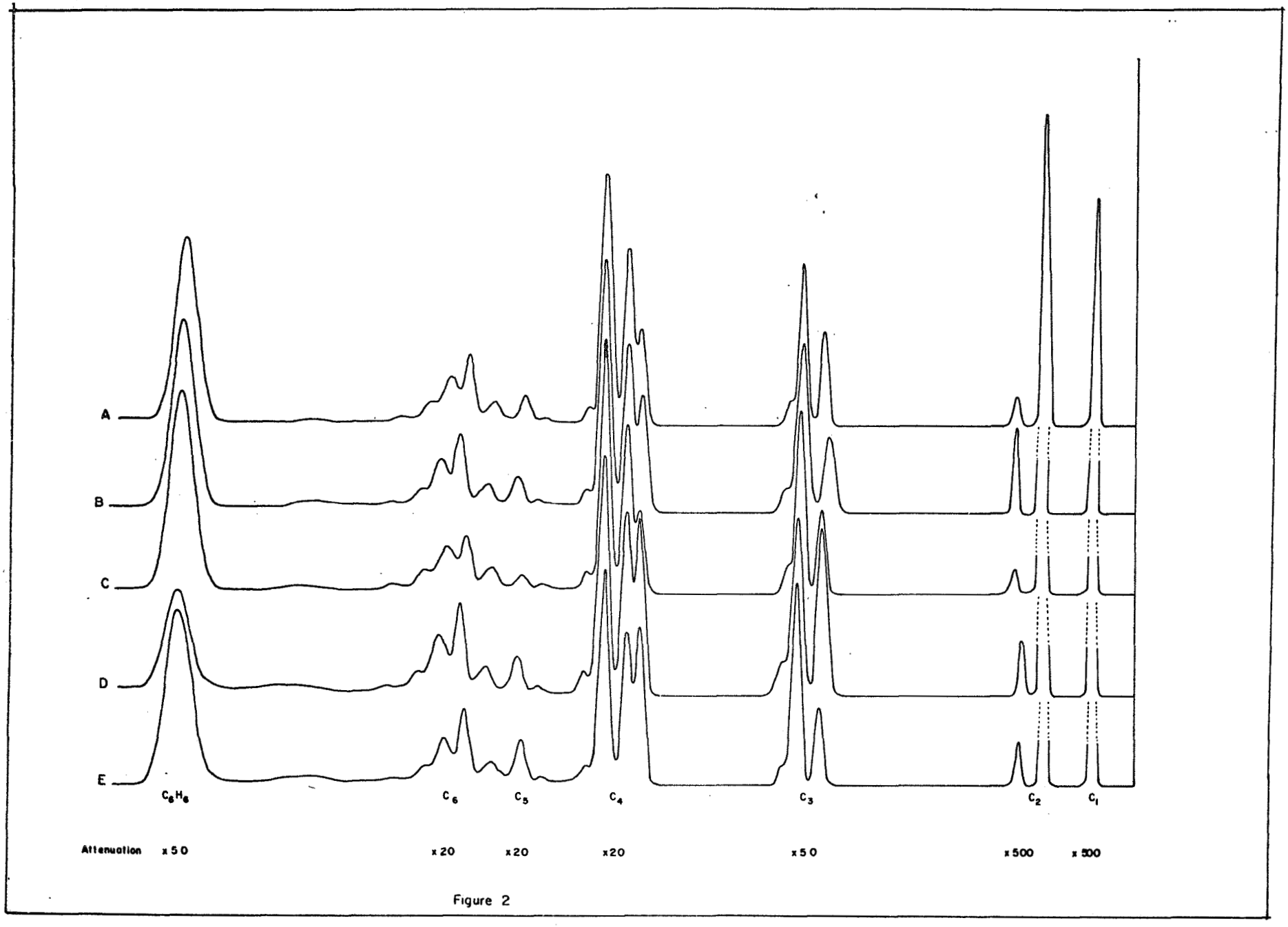
A
B
C
D
E
$C_6H_6$
$C_6$
$C_5$
$C_4$
$C_3$
$C_2$
$C_1$
Attenuation
x 5 0
x 20
x 20
x20
x 5 0
x 500
x 500

Figure 2

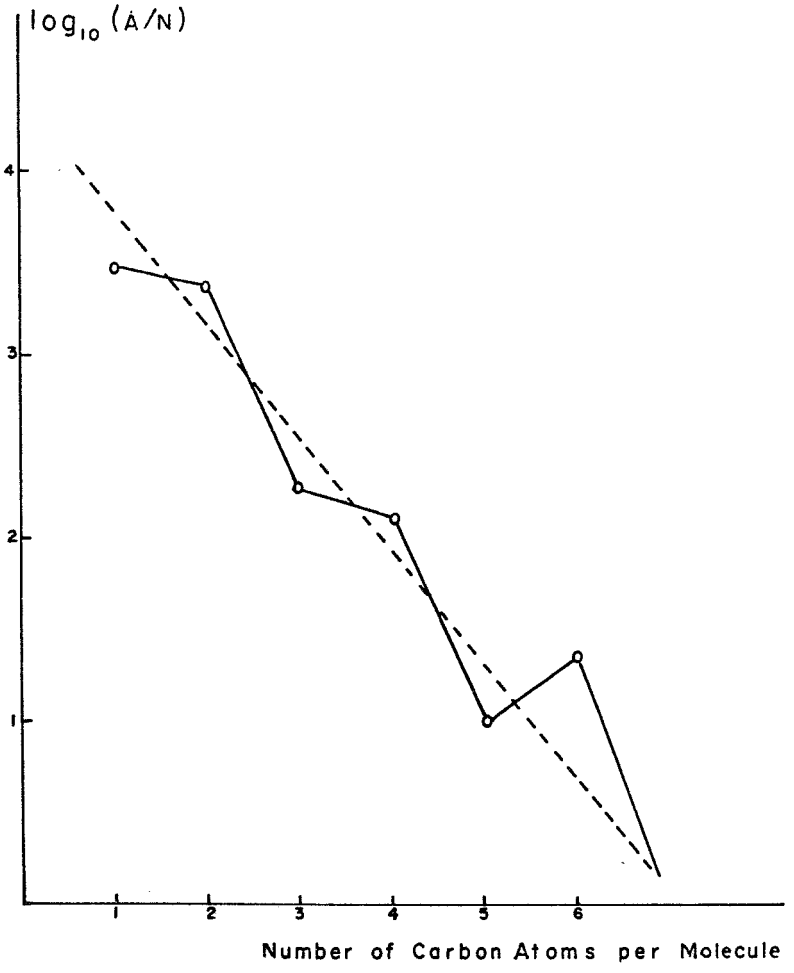


Figure 3

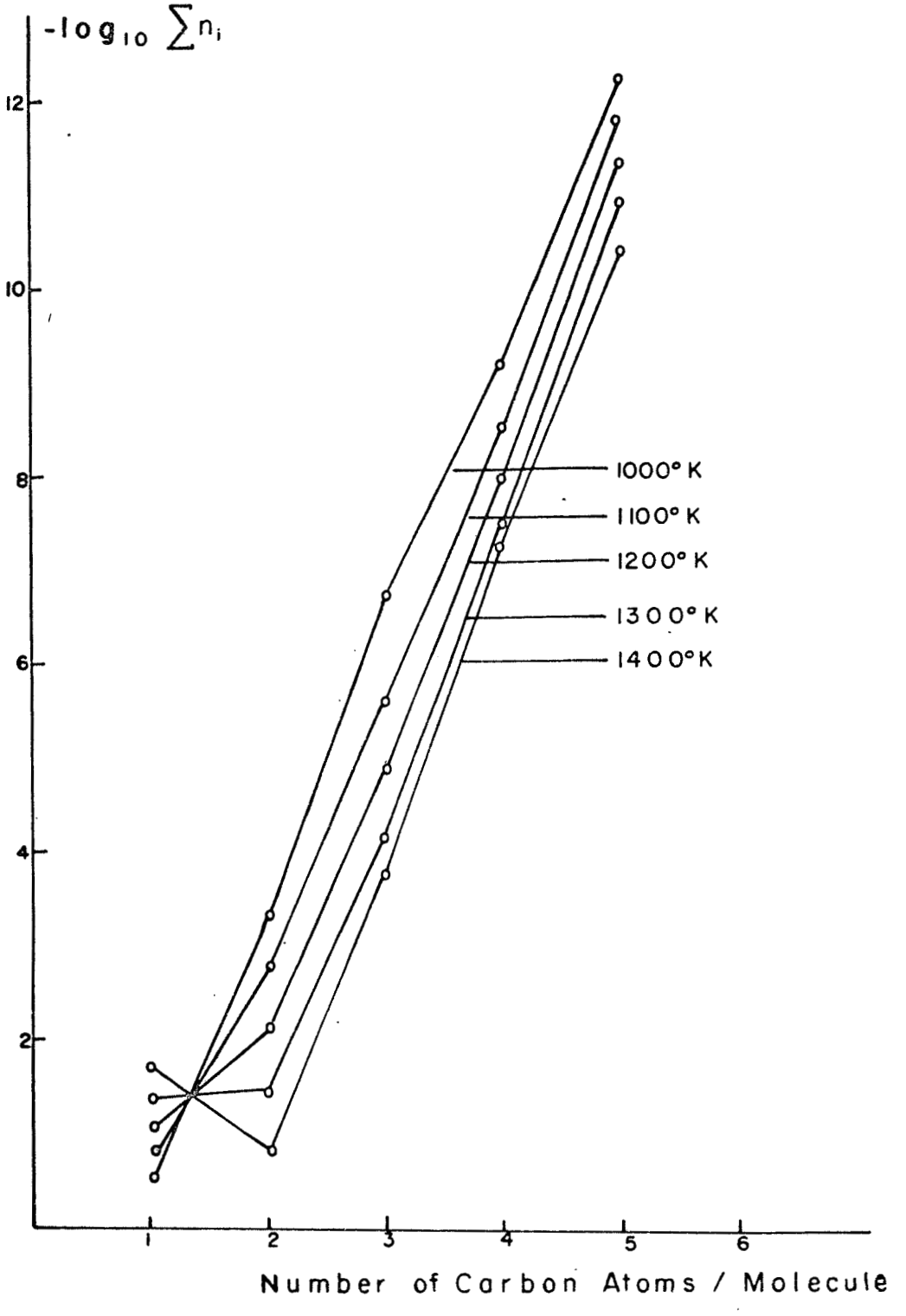
$-\log_{10} \sum n_i$
12
10
8
6
4
2
1000° K
1100° K
1200° K
1300° K
1400° K
1
2
3
4
5
6
Number of Carbon Atoms / Molecule

Figure 4

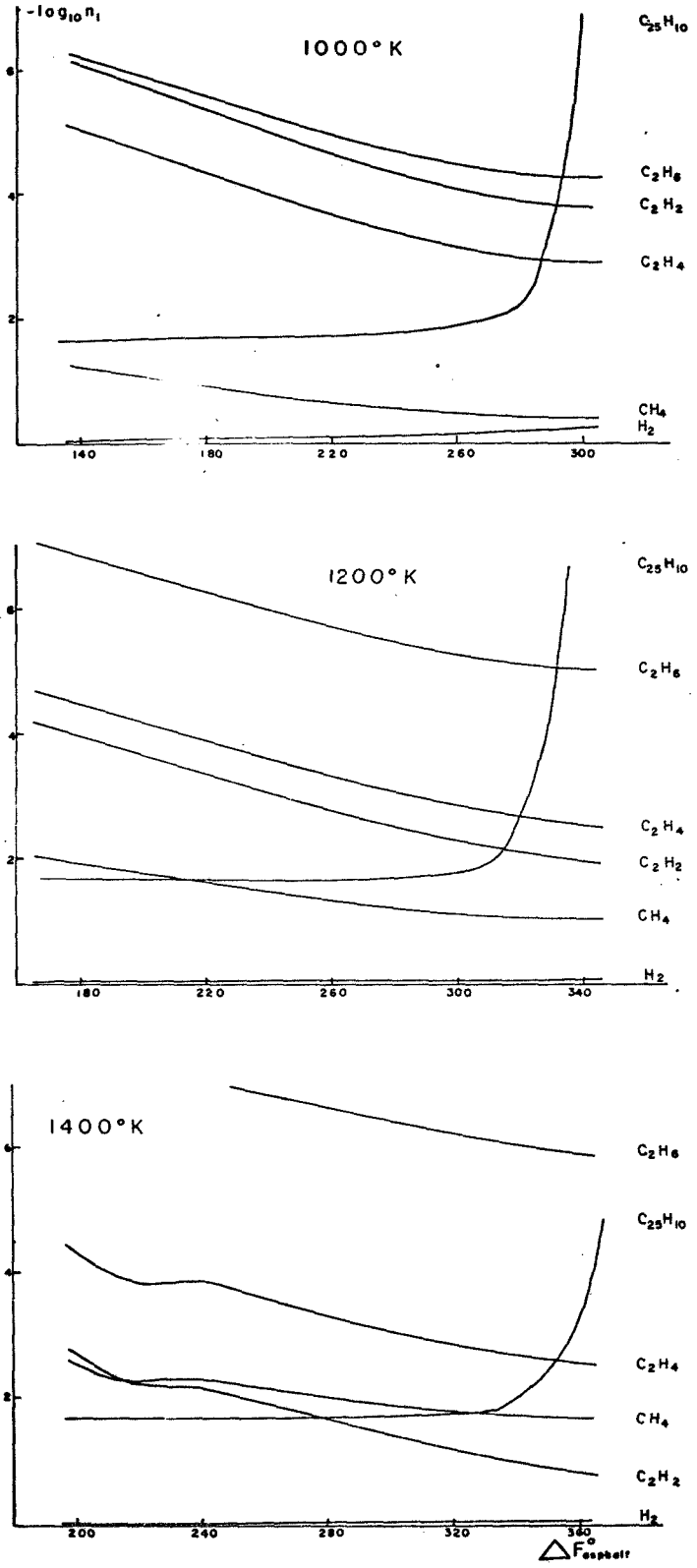
-log10 ni
1000° K
C25H10
C2H6
C2H2
C2H4
CH4
H2
140
180
220
260
300
1200° K
C25H10
C2H6
C2H4
C2H2
CH4
H2
180
220
260
300
340
1400° K
C2H6
C25H10
C2H4
CH4
C2H2
H2
200
240
280
320
360
ΔF°asphalt

Figure 5

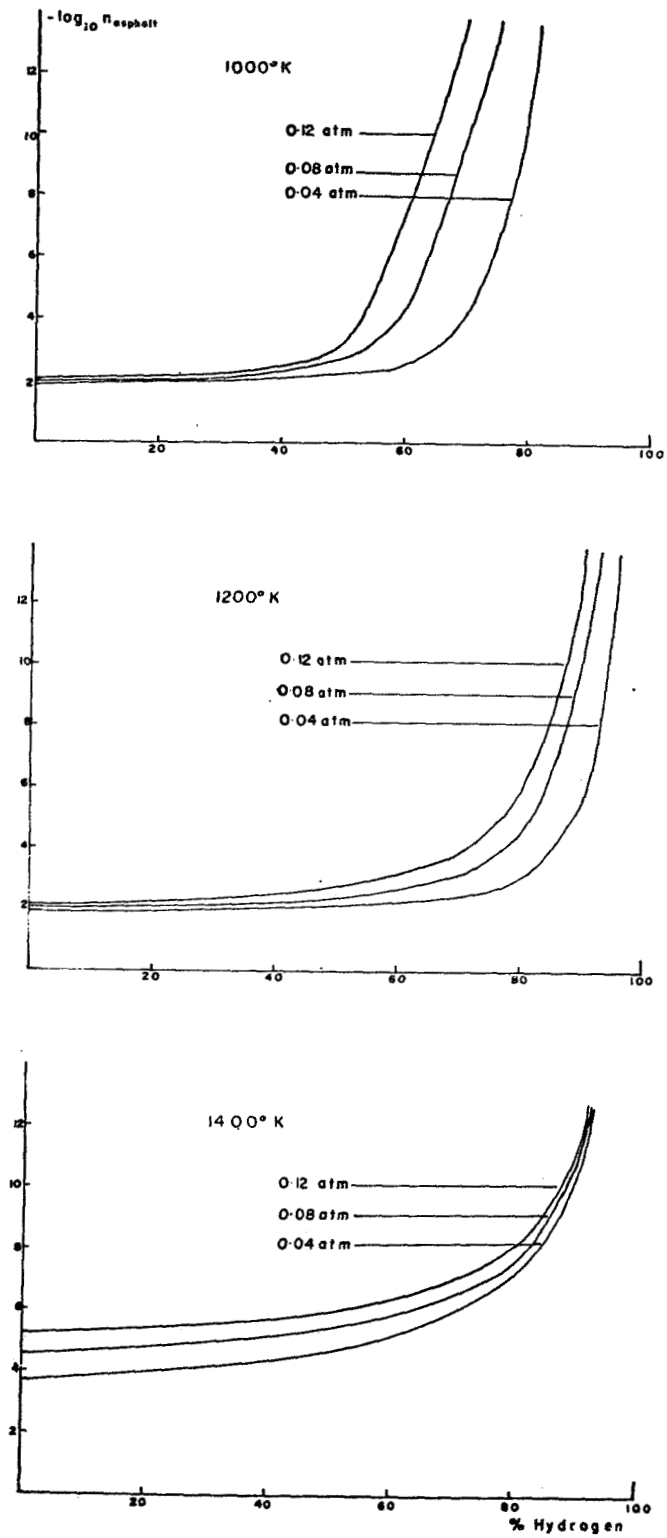
$-\log_{10} n_{asphalt}$
1000° K
0·12 atm
0·08 atm
0·04 atm
1200° K
0·12 atm
0·08 atm
0·04 atm
1400° K
0·12 atm
0·08 atm
0·04 atm
% Hydrogen

Figure 6

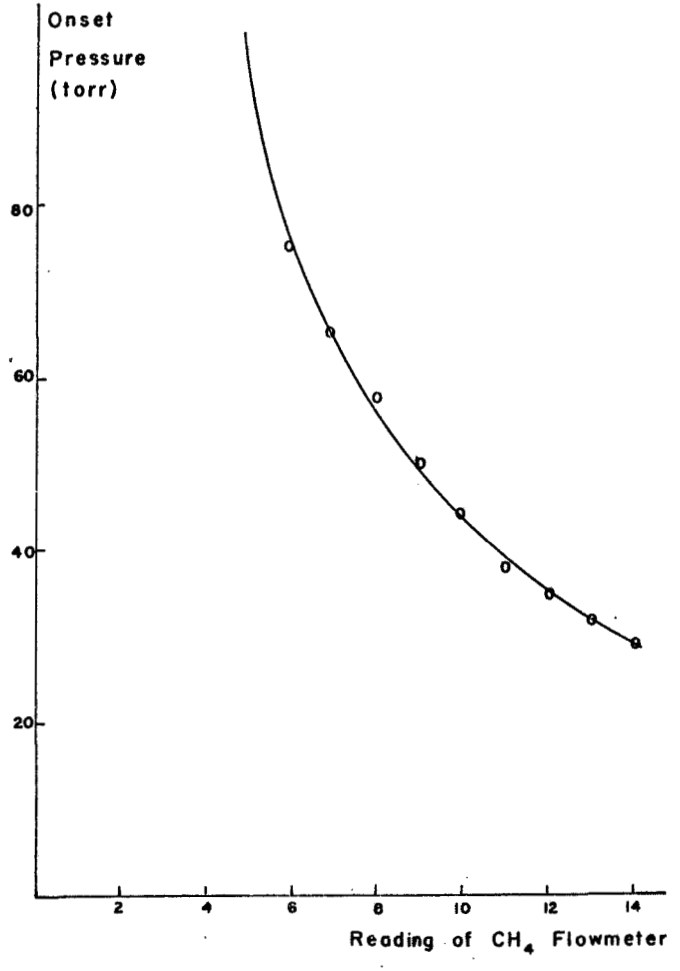
Onset
Pressure
(torr)
80
60
40
20
2
4
6
8
10
12
14
Reading of $CH_4$ Flowmeter

Figure 7

## LIST OF FIGURES


Figure 1 The Change in Calculated concentration of the major products with the elemental composition of the starting gases.

Figure 2 Gas Chromatograms of the product gases, measured using a six foot column of Parapak Q with temperature programming to 170°C; A-E represent the starting elemental compositions.

Figure 3 The variation of the total equilibrium concentration of all the hydrocarbons from $C_1$ to $C_5$ with the number of carbon atoms per molecule.

Figure 4 The experimentally determined variation of the concentration of the hydrocarbons from $C_1$ to $C_6$ with the number of carbon atoms per molecule.

Figure 5 The variation of the computed concentration of the major products with the free energy of formation of asphalt, $C_{25}H_{10}$.

Figure 6 The variation of the equilibrium mole fraction of asphalt in mixtures of hydrogen and methane.

Figure 7 The variation of the pressure at which the glow discharge changed to a flame plasma with the flow rate of methane; the reading of the hydrogen flowmeter was kept constant at 15.